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Hot Water Extraction Technology (HWE) On-Site Remedial Technology for Contaminated Soils and Sediments

By Indira S. Jayaweera, SRI International





INTRODUCTION

In 1999, DOE's National Petroleum Technology Office (NPTO) funded SRI International to develop and evaluate a hydrothermal extraction technology (or hot water extraction technology [HWE]) for remediating petroleum-contaminated soils. The project is in its final stages, and the bench-scale demonstration of the process has shown great promise. The implementation of this technology will revolutionize the conventional use of water in soil remediation technologies and will provide a stand-alone technology for removal of both volatile and heavy components from contaminated soil.

BACKGROUND

During operations related to recovery, refining, and transport of oil from domestic sources, contamination of soil, air, and ground water is inevitable. The soil contamination results primarily from (1) drilling operations in which drilling fluid becomes contaminated in the reserve pit during and/or after completion of the well; (2) production operations in which oil, condensate, or produced water are spilled or released into the ground; and (3) pipeline breaks or leaks that release crude oil and/or produced water into the soil. Clean-up operations for environmental compliance add significantly to the operation costs of domestic oil production. In many cases,

Contents

- 5 Air Quality Research at Lawrence Berkeley National Laboratory Studies target the West Coast and Rocky Mountains
- 9 Environmental Compliance Assistance Website Guidelines to meeting Federal regulations
- **12** Calendar

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intrinsic biochemical remediation, which is one of the least expensive soil remediation methods, is either ineffective because of high concentrations of contaminants or too slow. Other remediation alternatives can be very expensive. This remediation barrier has contributed to the continuous decline of U.S. crude oil production, which in turn has increased our dependency on foreign supplies. Therefore, to lower production costs and to maintain access to domestic resources, we need improvements in existing technologies or new technologies for soil and water remediation.

Biodegradation, bioventing, pyrolysis, solvent extraction, thermal desorption and incineration are some of the in-situ and ex-situ technologies currently available for soil remediation. However, most current remediation practices either (1) cost too much, (2) fail to remove all the polycyclic aromatic hydrocarbons (PAHs) found in petroleumcontaminated sites, or (3) require the use of organic solvents to remove contaminants, at the expense of additional contamination and with the added cost of recycling solvents. Alternative innovations must be more economical and efficient, meet environmental regulatory requirements, and gain public acceptance. Hydrothermal extraction offers the promise of efficiently extracting PAHs and other kinds of organics from contaminated soils at moderate temperatures and pressures.

SRI APPROACH

In remediating soil contaminated with oil, separation technologies are better than destruction technologies because the pollutant itself may not be hazardous and the heat value of the recovered fuel can be used to compensate the cost of the remediation process. Therefore, to remediate soil contaminated with petroleum compounds, solvent extraction seems to be more appropriate. However, if organic solvents are used for either exsitu or in-situ remediation, the removal or disposal of the used solvent is a problem. These solvents may be volatile, causing secondary pollution. One way to minimize the secondary pollution is to find substitutes for organic solvents that are less hazardous to the environment.

SRI is developing an advanced hydrothermal technology to separate the petroleum-related contaminants and other hazardous pollutants from soil and sediments. In this process, water with added electrolytes (inexpensive and environmentally friendly) is used as the extracting solvent under subcritical conditions (150 °C-300 °C). The use of electrolytes allows us to operate reactors under mild conditions and to obtain high separation efficiencies that were hitherto impossible. Also, the importance of water as a solvent is that, unlike common organic solvents, water under subcritical conditions dissolves both organics and inorganics, thus allowing opportunities for separation of both organic and inorganic material from soil.

TECHNICAL DEVELOPMENT

In developing this technology, our systematic approach was to establish fundamental solubility data, conduct treatability studies with industrial soils, and perform a bench-scale demonstration using a highly contaminated soil. Initial work was conducted with selected PAHs, which are difficult to remove from soil to measure solubility under hydrothermal extraction conditions. Figure 1 depicts the measured solubilities for pyrene, fluoranthene, chrysene and 9,10-dimethylanthracene in high-temperature water using SRI's hydrothermal optical cell. No literature data are available on in-situ measurements of solubilities of PAHs, and to our knowledge, this is the first recording of solu-

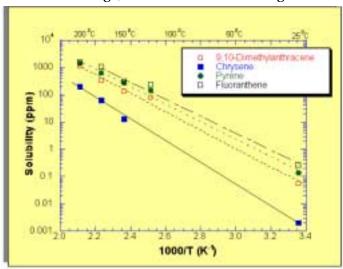


Figure 1. Solubility of PAH in water in temperature range RT-200 °C.

bility data for PAHs measured under hydrothermal conditions by in-situ measurements. The solubilities of all the tested PAHs in water increase with temperature. Compared with the reported solubilities at room temperature, the values obtained are 900-3,600,000 times higher, depending on the temperature and the PAH selected. These solubility data help determine the appropriate conditions for our treatability studies with contaminated soil.

To conduct the treatability studies, SRI used several different industrial soils (e.g., Tallman Oil Company site, Colorado, and an organic wood preserving site in the Northwestern United States) and EPA-certified soils for evaluating the effectiveness of hydrothermal extraction. Collectively, these samples contained benzene, ethylbenzene, toluene, BETEX pentachlorophenol (PCP), creosote and 20 different PAHs. The removal efficiency for the industrial samples was very promising, with a greater than 99.9999% removal of PAHs, including benzo(a)pyrene under HWE conditions. Table 1 shows the treatment performance data evaluated from the treatability study for selected PAHs in an EPA-certified soil containing semivolatiles and PAHs.

The bench-scale demonstration was performed using drilling mud obtained from a site in Mexico. This mud contained 20% TPH (total petroleum hydrocarbon), including heavy components. Since this sample contained large amounts of volatiles, we were able to assess the ability of the HWE technology to recover the volatiles for reuse as a fuel and reduce the energy cost. Figure 2 is a photograph of the bench-scale reactor system designed for this demonstration. Figure 3 shows a block flow diagram of the process, along with photographs of oil-drilling mud and its cleaning stages. In this process, mud is injected into the reactor along with the preheated water. In the reactor, volatile hydrocarbons are first separated from the mud, then recovered for reuse and to use as fuel for heating water. The semivolatiles and PAHs are then removed to obtain ultra-clean soil. We were able to exceed the cleanup goal, 200 mg/kg TPH, specified for this site. The temperature and pressure ranges used in the process were 50 °C-250 °C and 3-50 atmospheres, respectively.

FAR	Maximum Untreated soil Concentration (mg/kg)	HWE Treated Sail Consectration (reging)	
Hapfetianne:	361.	HD(403)	
Prenanthrane	1904.9	ND (483)	
Fluoromere	1400 II	HD (40.2)	
Pyrene	1075.1	ND(+0.2)	
Chrysene	310.t	HD (40.0)	
Benzojacpenene	96.5	MDIKESI	

Table 1. Treatment performance data for selected PAH's.

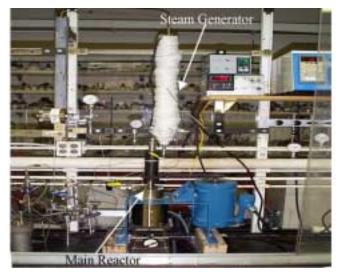


Figure 2. Bench-scale reactor system for treatability studies.

PILOT DEMONSTRATION

The next step of the development process is the successful pilot demonstration of this technology. Once pilot tested, this technology can be implemented quite easily, since most of the basic components are readily available from mature technologies (e.g., steam stripping, soil washing, thermal description). We believe a 1 ton/hr pilot-scale plant would be ideal for demonstrating this technology. It could be used in field testing operations as a mobile plant that can be moved from site to site for site restorations. It would also be easy to scale up the design for large stationary plants (40-100 ton/hr). SRI is currently evaluating the preliminary engineering parameters from our data obtained from bench-scale testing. Preliminary

estimates indicate that the cost of cleaning soil using the SRI process may vary from \$200-300/ton.

SRI is seeking partnership opportunities with DOE and industry for successful pilot demonstration of this technology.

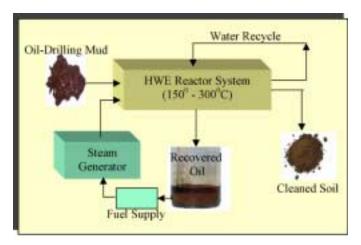


Figure 3. A simplified version of HWE process flow diagram.

ACKNOWLEDGMENTS

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DOE Project Manager: Nancy Comstock. SRI Project Team: Indira Jayaweera, Montserrat Marti-Perez, Jordi Ferrero, Victor Ramayrat, Gopala Krishnan, and Angel Sanjurjo.



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Contacts for DOE's Oil and Gas Environmental Program:

Herb Tiedemann Herb.Tiedemann@npto.doe.gov 918-699-2017

Nancy Comstock Nancy.Comstock@npto.doe.gov 918-699-2059

Editor:

Viola Rawn-Schatzinger Viola.Schatzinger@npto.doe.gov 918-699-2018

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U.S. Department of Energy
National Energy
Technology Laboratory
National Petroleum Technology Office
One West Third Street
Tulsa, OK 74103-3519



Air Quality Research at Lawrence Berkeley National Laboratory

By Nancy J. Brown, Lawrence Berkeley National Laboratory

The Regulatory Situation

Exploration and production (E&P) of petroleum is frequently conducted in relatively remote areas (e.g., the North Slope), but can also be active in populated areas (e.g., Houston, Bakersfield). Sources tend to be concentrated geographically: thus, their impacts may be aggregated. Today, concern about E&P emissions is focused on five or six areas in the United States where operations are ongoing. In light of the concerns about air quality degradation and current or potential future exceedances of the standards, as well as concern for air quality-related values, the impacts of E&P operations on air quality merit attention. E&P sources emit semi-volatile organic compounds (SVOC), volatile organic compounds (VOC), NOx, SO₂, CO, fine particles (PM-10 and PM-2.5, total mass of particles sized 10 and 2.5 microns and less, respectively), and air toxics. SVOC, VOC,

NOx, and SO₂ participate in the formation of particles consisting of sulfates, nitrates, and secondary organic compounds, which contribute to aerosol loading, visibility impairment, and acid deposition. Some constituents of SVOCs and VOCs are also listed as air toxics. CO can build up to significant levels in very cold climates, such as the North Slope, due to the extreme stability of the atmosphere and the complete suppression of vertical mixing at very low temperatures and under calm wind conditions. Table I delineates the pollution issues now faced, or that may potentially arise in the future, in major production areas.

The legislative basis for air pollution abatement in the United States is the 1963 Clean Air Act (CAA) and its subsequent amendments. Major amendments were made in 1970, 1977, and 1990. The law establishes the federal-state relationship that requires the EPA to establish National Ambient Air Quality Standards (NAAQS), and empowers the

Pollutant or impairment	Gulf Coast	North Slope	San Joaquin Valley	Rocky Mountain Region	California Coast
Visibility	A concern	An issue	Serious impairment in summer and winter	Degradation a serious concern	A possible concern
SO ₂ , sulfate				A concern	
Ozone	A serious concern		A serious concern	A potential issue under new standard	A concern
Acid Deposition				A new issue and serious concern	
PM-10; PM-2.5	A concern		A serious concern	Potentially an issue	A potential concern
CO		A concern			

Table I. Current pollution issues faced by the Oil and Gas Industries.

states to implement and enforce regulations to attain them. The CAA requires each state to adopt a plan, a so-called State Implementation Plan (SIP) that provides for the implementation, maintenance, and enforcement of the NAAQS. Six criteria pollutants are identified: sulfur dioxide (SO₂), particulate matter (PM-10 and PM-2.5), nitrogen dioxide (NO₂), carbon monoxide (CO), ozone (O₃), and lead. The major reason for amending the CAA was the failure to bring areas that were out of compliance into compliance according to a preset schedule.

Ozone, Air Quality Models, and Uncertainty

As is widely known, a great deal of effort has been directed toward reducing tropospheric ozone concentrations in the U.S during the past 25 years. Significant improvements have been achieved, but the standard is still exceeded in a large number of metropolitan areas in the country. In 1997, the U.S. EPA promulgated a new ozone standard (Shell, 1998), lengthening the averaging time from one to eight hours, and tightening the concentration limit from 120 to 80 ppmv (parts per million by volume). Analyses suggest that far more areas will exceed the new standard than the current one, and that reducing ozone in rural and "non-peak" urban areas may prove to be quite challenging. E&P sources tend to be located in these newly affected challenging locations.

Reducing ozone is challenging because ozone is a secondary pollutant, formed in the atmosphere by reactions between other pollutant gasses (primarily NOx and VOC) driven by sunlight. Ozone concentrations are a complex function of NOx and VOC concentrations as well as meteorological conditions. Ozone reduction strategies throughout the U.S. have targeted reducing VOC concentrations, while some locations, e.g., California and the Northeast, require reductions of both VOCs and NOx concentrations. The issue of control strategies has been recently revisited to determine whether, and under what circumstances, controlling one or both of the ozone precursor pollutants is warranted. It appears from the NARSTO (North Atlantic Research and Study of Tropospheric Ozone) assessments that we might anticipate more NOx control in the future.

Photochemical Air Quality Simulation Models (PAQSM) are used extensively in preparing State Implementation Plans to describe how an area out of compliance with ozone or other air quality standards will be brought into compliance. Photochemical air quality simulation models (actually, modeling systems) are used to estimate the concentrations of secondary pollutants downwind of individual E&P sources and aggregates of sources. The PAQSM may be used to assess the contributions of these sources to overall air quality in the downwind area, recognizing that other categories of sources may contribute as well. The models might also be used to assess the relative contributions to air quality of individual E&P sources that are part of an aggregation of sources, and to determine the air quality benefits in the downwind area of reductions in emissions from individual sources or groups of sources.

Errors and uncertainties are inherent in any modeling system through errors in theory, observations, approximations, and precision. Thus, uncertainties resulting from these categories will be present in the modeling exercises conducted to evaluate E&P impacts. Figure 1 shows how uncertainties in an input parameter can affect model output. In the figure, the input parameter ${\bf a}$ is characterized by a range of values indicated by $P({\bf a})$ which results in a range of values for the output variable $f({\bf a})$. In recognition of the importance

of quantifying uncertainty for making more informed decisions. Lawrence Berkeley National Laboratory (LBNL) is conducting research whose objective is to provide tools and capabilities for estimating uncertainties in

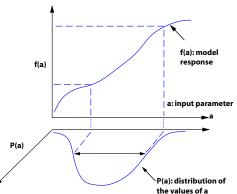


Figure 1. The range of uncertainty in model output due to uncertainty in the parameter **a** is indicated by f(**a**). The most probable values of model output are enclosed between the dotted lines.

PAQSM. Their research is focused on developing a framework, algorithms, and computer codes for estimating modeling uncertainties, as well as conducting prototype applications. In addition, effort is also directed, through interviews with stakeholders and decision makers, towards identifying a better approach for communicating uncertainty information so that it might be used by the air quality policy and planning community as a valuable tool in decision making.

The researchers at LBNL have developed a prototype version of an uncertainty framework, shown schematically in Figure 2. Note in particular the many linkages between the elements of the framework. Execution of the framework begins with data collection for both model inputs and performance evaluation. The model is selected according to the problem at hand, and a modeling protocol is designed whereby metrics for performance evaluation are identified. Operational evaluation involves comparing predictions with observations to generate statistical summaries of error and bias. Diagnostic evaluation is the examination of specific modeling components or responses of the model to dynamic change. Sensitivity analysis involves estimating the responses of outputs to variations in the inputs, and can be used to explore relationships among variables and to estimate output uncertainty due to uncertainties in input parameters. Corroborative Analysis is the comparison of model outputs with results from observation-based models, alternative models, or other independent means. These four types of analyses are used in concert to evaluate whether model performance is satisfactory, and to identify areas most important for model improvements.

Previous research employing sensitivity analysis revealed that uncertainties in ozone prediction are most strongly correlated with uncertainties in NO₂ photolysis rates. Photolysis rates depend on available solar (actinic) flux. As sunlight enters the atmosphere, a portion of the light is extinguished by scattering and absorption from gases and particles in the atmosphere. This extinguished light in not available to drive the photochemistry. Optical depth is a measurement of light extinction along a vertical path, and the single scattering albedo

(SSA) represents the fraction of extinguished light that is scattered. LBNL recently improved the description of the photochemistry in air quality modeling (under sponsorship of the California Air Resources Board) by adding a new submodel for radiative transfer and accounting for the effects of variability in atmospheric composition on the actinic flux. High concentrations of aerosol particles and ozone in the atmosphere increase the optical depth, and thereby reduce photolysis rates. Under DOE sponsorship, LBNL exercised parts of the framework described above to assess the uncertainty associated with these model improve-

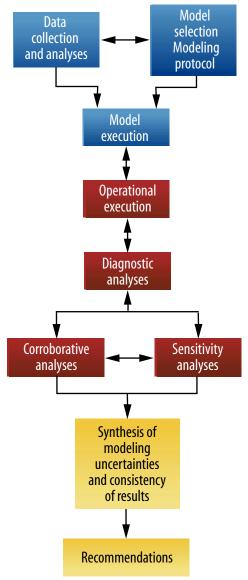


Figure 2. The initial framework for air quality model. Schematic shows model evaluation and uncertainty estimation.

ments. Figure 3 shows the ratio of predicted to observed values of the NO_2 photolysis rate for three values of the SSA. The ratio of predicted to observed NO_2 photolysis rate reveals an average bias of 17 to 36%. By employing corroborative analysis, the researchers were able to reduce the bias by determining that the SSA was actually in the range 0.77 to 0.85. Statistical analysis of the experimental data revealed a systematic error in part of the data that could be attributed to carrier gas impurities. By this careful analysis of the sources of uncertainty, the bias between the measured and predicted values was reduced to 10%. Current research is directed toward further applications of the uncertainty framework.

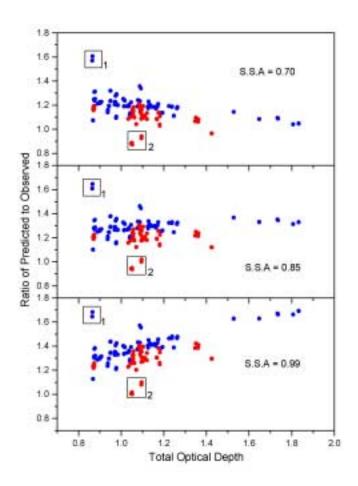


Figure 3. The ratio of predicted to observed values of the photolysis rate for three values of the Single Scattering Albedo (SSA) is plotted as a function of total optical depth. Accounting for the measurement errors reduced the bias in the ratio to 10%.

Particulate Matter and Health

Coincident with instituting an ozone standard, the U.S. EPA introduced a new fine particle standard, while retaining the current standard for PM-10. The new standard for fine particles, the so-called PM-2.5 standard, calls for the annual arithmetic mean of 24-hour samples not to exceed $15\mu g/m3$, and the 24-hour average not to exceed $65\mu g/m3$. Due to limited availability of data, less is known about the potential for exceeding the new standard. The DOE is interested in characterizing the impacts on air quality of both primary particles and secondary particles formed from emissions from E&P operations.

National Ambient Air Quality Standards for outdoor airborne PM-2.5 were established largely based upon epidemiological studies that found associations between outdoor particulate-matter concentrations and a number of adverse health effects. However, because individuals are indoors 80–90% of the time (70% in homes), determining indoor concentrations of outdoor particles is key to learning and accurately apportioning the health risks associated with PM-2.5. At present, regulatory standards have focused on the total mass of suspended particles, because there is no scientific evidence to implicate any particular size or chemical component of the particle population. Exposure to the important types of PM-2.5 must be determined and quantified for accurate apportionment of their associated health effects. Only then can controls be designed that actually will reduce risk.

At two California sites—the San Joaquin Valley (Fresno Field Site) and the San Francisco Bay area (Richmond Field Site) — LBNL project researchers are measuring concentrations of indoor and outdoor PM-2.5 under a wide variety of conditions to develop a physically based, semi-empirical predictive model of the transport and transformation processes affecting indoor PM-2.5 concentrations of outdoor origin. The model will be general enough to predict probability distributions for species-specific indoor concentrations of PM-2.5 (sulfate, nitrate, organic and black carbon constituents) based on outdoor PM and gas-phase species concentrations, meteorological conditions,

building construction characteristics, and heatingventilation-air conditioning (HVAC) conditions. The researchers have turned these field houses into laboratories by conducting a series of controlled experiments in which they systematically vary the parameters required to characterize the physical and chemical processes that occur when gases and particles cross the building shell.

Detailed field-based measurements are necessary to develop the model because particle characteristics and size/composition relationships change as they cross a building shell (Figure 4). Loss of particles through the building shell and deposition onto and possible reactions with residential contents will affect indoor PM concentrations. In addition, phase changes that depend on chemical composition and temperature can affect indoor PM concentrations. For example, the gas-to-particle partitioning of ammonium nitrate—the largest chemical mass constituent of PM-2.5 in many

areas of the Western United States—is highly dependent on factors such as temperature, and nitric acid and ammonia concentrations that change as outdoor air is transported indoors. To fully characterize this complex dynamic system, chemical speciation and particle sizing measurements of both outdoor and indoor PM-2.5 have been conducted. Fortunately, some of the non-volatile chemical components of outdoor PM-2.5, such as sulfate, have no common indoor sources and thus provide an excellent means to trace transport of outdoor PM-2.5 into indoor air.

Project research is being performed in collaboration with other investigators in the California Regional Particulate Air Quality Study (CRPAQS) to benefit from their multi-year, multi-institutional detailed and intensive outdoor air study. Two intensive field campaigns were conducted at the Fresno field site, one in the summer-fall of 2000 and the other in the winter of 2000-2001. Each

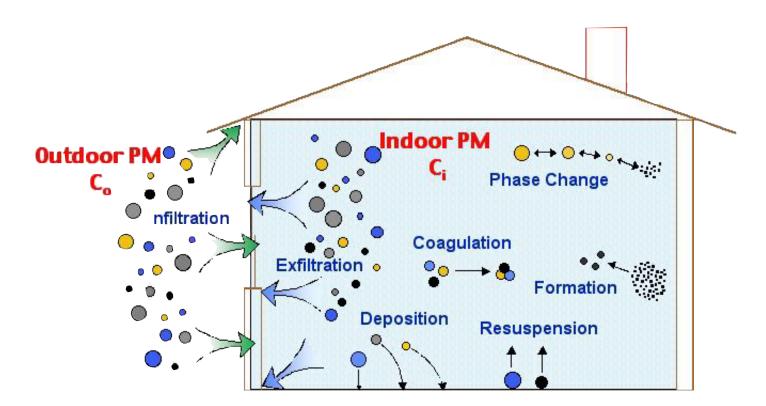


Figure 4. Particles enter and leave a house with air infiltrating and exfiltrating through cracks and leaks in the building shell. Once inside, particles undergo physical and chemical transformation processes due to the differences between the indoor and outdoor environment. Two of the more important processes are particle deposition to indoor surfaces and phase changes in a gas-particle equilibrium.

lasted two weeks and data collection was continuous. The instruments used for these field studies provide near real time (5-30 minute) measurements of the particle size distribution, chemically resolved PM-2.5, and gas phase ammonia and nitric acid. A new instrument developed by team researchers at Aerosol Dynamics Incorporated was used to provide automated 10-minute resolution monitoring of fine-particle nitrate, sulfate, and carbonaceous aerosols in indoor and outdoor environments. In addition, researchers at LBNL have created a system for the simultaneous measurement of indoor and outdoor ammonia and nitric acid at 30-minute time intervals with subppb sensitivity. Several models of traditional particle measurement instruments were employed to characterize the particles, and 12-hour filter measurements were performed to provide integral measures of particle mass and chemical constitution. Characterization of the infiltration rate and forces that drive infiltration (e.g. temperature and pressure differences across the building shell) were also performed.

The use of multiple instruments to provide simultaneous indoor and outdoor measurements has provided a rich data set that will enable significant improvements in our understanding of the physical and chemical factors influencing the indoor concentration of particles of outdoor origin. Preliminary investigation of the data demonstrates that the house measurements track the particle concentrations measured at a local metropolitan regional air quality monitoring station. The results further indicate that indoor/outdoor concentration ratios of different chemical species and different size cuts vary significantly as illustrated in Figure 5. These results strongly imply that measurement of PM mass is not adequate for determining exposure - speciated measurements are required.

Broad application of the model for indoor particulate matter requires that the infiltration rate can be predicted based on readily measured properties of the housing stock (e.g. leakage areas) and regional meteorological characteristics. LBNL has recently completed a comparison of the measured infiltration rates obtained from the Fresno field house

with model predictions obtained using the LBNL/AIM infiltration model. The infiltration rate was measured with approximately hourly resolution using a constant SF₆ release tracer method. The comparison between measured and modeled infiltration rates for a non-intensive period in December 2000 is quite good. In particular the model captures the diurnal variation in air infiltration rate due to temperature and wind load infiltration driving factors. Based on this good agreement, LBNL expects to be able to combine the predictive capability for infiltration rate with the experimental results to produce a final particulate matter model that is applicable to the larger housing stock. In the future, this model will be tested against field measurements made in a suite of residential buildings. Credibility of the model will be evaluated and established with respect to its realworld representation, accuracy, and limits of prediction. The methodology, tools, data, and models derived from this study will also benefit air quality efforts in other areas of the United States.

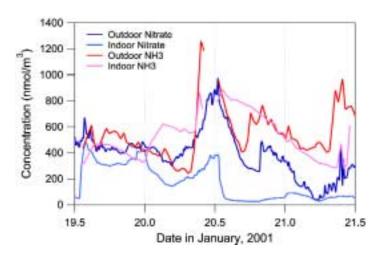


Figure 5. High-time resolution measurements of the concentration of both ammonium nitrate particles and gaseous ammonia outdoors and within the residence. Note how well correlated the outdoor ammonia and ammonium nitrate measurements are, particularly on Jan 20th. The indoor environment was manipulated for each of the four 12-hour periods as follows: 1) air exchange rate (ACH) 4 h⁻¹ with heat off, 2) ACH 5 h⁻¹ with heat on, 3) ACH 0.3 h⁻¹ with heat off, and 4) ACH 1 h⁻¹ with heat off. When the heat is turned on there is a sharp decrease in indoor ammonia nitrate particles and an increase in indoor gas phase ammonia, indicating a shift from particle to gas phase.

Particulate Matter and Visibility

Another important effect of particulate air pollution is visibility impairment, which is of particular concern in national parks and pristine (or Class I) areas such as the Bridger Wilderness located in southwestern Wyoming. Visibility impairment is a "value" associated with air quality, distinguished in regulation from ambient measures of air quality. The distinction between direct ambient measures and values is important because regulatory requirements for attaining and maintaining air quality (i.e., NAAQS) are very different, more explicitly defined, and in many ways more stringent, than requirements for preserving air qualityrelated values (e.g., visibility).



Figure 6. Map showing monitoring sites in Wyoming. The three IMPROVE monitoring sites are designated by stars, and they are part of a network of sites used to assess visibility. The CASNET (Clean Air Status and Trends Network) sites are collocated with the IMPROVE sites, and they are used to provide the nations primary source for atmospheric data to estimate dry acidic deposition and concentrations of ozone in rural areas. Airborne particles are measured at the 11 SLAMS (State and Local Air Monitoring Stations), designated by squares and operated by the EPA. The NADP (National Atmospheric Deposition Program) focuses on monitoring acid deposition, and there are eight active sites in Wyoming designated by open circles.

Wyoming as a prototype for the region. This research is important because current and future development of energy resources in the region could impact regional haze. Initial efforts involved analyzing the available data to support understanding the scientific issues including the databases for air quality, visibility, meteorology, and emissions, and how these items affect the modeling system used to apportion visibility impacts. They have also analyzed the current regulatory context, and identified scientific issues that are important to understand in the regional haze debate.

Wyoming and much of the Central Rocky region have very clean atmos-

pheres, and as a result have very few monitoring and emissions data sets. The sites where monitoring does occur in Wyoming are shown in Figure 6. This paucity of data makes air quality modeling very difficult since there are insufficient data for creating model input files and evaluating modeling performance. Recent research has involved identifying appropriate modeling, analyses, and monitoring approaches for characterizing industry's contributions to visibility degradation. Future research will be concerned with contributing to the science base required for model improvements and for determining model performance.

Current LBNL effort involves statistical analyses of the IMPROVE (Interagency Monitoring of Protected Visual Environments) data using traditional statistical measures and time series analysis. The effort is Wyoming has been concerned with

Visibility is a complex function of physical stimulus variables, physiological processes, and psychological factors, all of which interact to determine the appearance of visual display. When a natural feature, for example, a mountain is viewed against a sky background, it is contrast between the mountain and the sky that makes it distinguishable. This contrast decreases with increasing pollutant load due to the extinction of the light passing between the object (e.g., the mountain) and the observer. Note that a natural amount of scattering from air molecules always exists, and is termed Rayleigh scattering.

EPA has recently written a new regional haze rule that impacts visibility in Class I areas. LBNL has been investigating visibility in Class I areas in



Figure 7. Pie diagram on the left illustrates the aerosol mass budget for Bridger Wilderness Area in southwest Wyoming. The data are collected at the IMPROVE monitoring station and are averaged for the period 1988 to 1995. Diagram on the right represents the aerosol extinction budget for the Bridger Wilderness area. The extinction budget based on both the mass budget and the mass scattering efficiencies for the aerosols and gases contributing to the extinction.

correlating visibility to measured. The average extinction budget averaged over many years for the Bridger Wilderness is shown in Figure 7. Note that sulfate and nitrate contribute a larger amount to the extinction budget than the mass budget. This is due to the fact that these chemical species are more efficient scatters combined with the effect of water uptake on light scattering for these species. Both fine soil and coarse mass, which make up a significant fraction of the aerosol, greatly decrease in significance in the extinction budget. It is worth noting that a large percent of the extinction is due to Rayleigh scattering, which indicates a relatively clean atmosphere.

Emissions research is another focus of the LBNL effort. They have developed a sampler for accurate measurements of reactive organic hydrocarbons from heavy crude oils. They have worked successfully with regulators and industry groups to write rules for emissions measurements for oil storage tanks. A new program to determine fugitive hydrocarbon emissions from refineries, chemical plants, and pipelines has recently been initiated. Researchers are currently developing new methods for measuring emissions associated with flashing losses. The emissions research results will be used by LBNL scientists, industry representatives, and regulators to develop the oil industry contributions to the emissions inventory for the

San Joaquin Valley for the California State Implementation Plan.

Concerns about E&P emissions are attributable, in part, to the introduction of new and more stringent air quality standards. But also contributing to concern is the projected substantial increased production of petroleum in future years, including an increased potential for natural gas production driven by air quality and global climate considerations.. The net result of increasing production will inevitably be increasing emissions of pollutants. This outcome, coupled with the new stringency of regulations, compels that attention be directed to documenting the sources and magnitudes of emissions. This effort includes estimating future emissions trends, assessing the impacts of current and projected emissions on air quality, identifying sources that need to be controlled, selecting technologies for effecting the controls, and assessing the likely air pollution outcome of instituting controls.

The DOE continues to identify important scientific questions that derive from laws and regulations. This includes tracking the rather generic issues, asking pertinent questions regarding decision-making authority, and identifying the required scientific capabilities to contribute to the resolution of complex environmental air quality issues.

DOE Announces the Environmental Compliance Assistance (ECAS) Website

The Environmental Compliance Assistance System (ECAS) is sponsored by the U. S. Department of Energy (DOE), National Energy Technology Laboratory's (NETL) National Petroleum Technology Office (NPTO). The purpose of the ECAS website is to provide the Oil and Gas industry with a tool that:

- Provides web links, phone numbers, and addresses of state and federal regulatory agencies where detailed information and forms may be obtained.
- Provides guidance on preparing waste management plans, records management, and emergency response issues.
- Presents current national and NPTO events relating to the Oil and Gas Industry.

This website should not be used as a sole source of information when evaluating compliance issues. Laws and regulations change, so we encourage you to check with regulatory authorities for further information. For additional information contact:

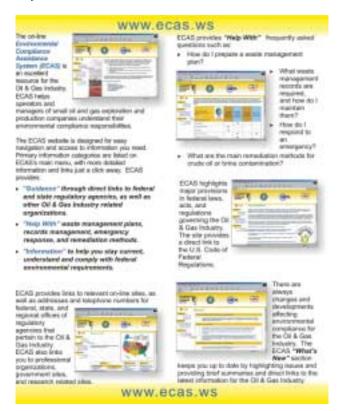
Ms. Nancy Comstock
Environment Project Manager
National Petroleum Technology Office
E-mail: Nancy.Comstock@npto.doe.gov

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Preparing a Waste Management Plan
Records Management
Emergency Response

Guidance Links

This section allows the reader to click on a map showing all the states and the ten EPA regions. Lists of state and regional agencies and contacts



for each area are given. A separate list gives the Federal regulatory and government sites including the Departments of Energy, Commerce, Interior, Environmental Projection Agency and others. Lists of professional organizations and industry related sites and research sites include a diversity of contacts including the American Association of Petroleum Geologists, Western States Petroleum Association, Petroleum Technology Transfer Council and the Hazardous Substance Management Research Center.

Preparing a Waste Management Plan

Ten step guidelines may be clicked with detail information on the following:

- Obtain Management Approval
- Define the Waste Management Plan Area
- Regulatory Analysis

- Waste identification
- Waste classification
- List and Evaluate Waste Management and Disposal Options
- Waste Minimization
- Select Preferred Waste Management Practices
- Prepare and Implement Area Waste Management Plan
- Review and Update Waste Management Plan

Records Management

Maintaining Records of Your Waste: It is important that operators minimize potential liabilities associated with off-site waste disposal by keeping records of the type, volume, analytical data, destination, transportation for all hazardous wastes. To simplify both record keeping and reporting, develop standardized forms with directions on how to complete the form with the required information.

The environmental compliance office should maintain the following records:

- Waste Analyses and Trial Tests
- Waste Inventory Log
- Inspection Records
- Manifests
- Exception Reports
- Maintain Exception Reports for at least three years.
- Legible copy of the manifest for which TSD confirmation has not been received.
- Cover letters which detail efforts taken to locate the waste and the results of those efforts.
- Land Ban Certifications
- TSD Notice of Waste Acceptance
- Certifications of Disposal
- Reporting retain copies of all reports submitted.

Emergency Response

Emergency response to an accidental release of a hazardous material will involve several steps. The following guidelines will assist you in making initial decisions upon arriving at the scene. However, you should not consider them to be a substitute for your own knowledge or judgment. These guidelines do not address all possible contingencies that may occur.

- Protective actions
- Identify the pollutants
- Federal and State regulatory contracts
- Record keeping and fulfilling reporting requirements

Protective Actions

Several protective actions should be carried out during an emergency response. In a case where the pollutant has not been identified the most important action would be to secure the area and call emergency personnel.

- First clear all personnel then, if possible, rope off the area.
- Get emergency help for any personnel affected by the spill.
- Based upon the injuries of any affected personnel, you might determine necessary evacuations even though the pollutant has not been identified.
- If you can stop the spread of the pollutant with out risk, do so.
- Shut off ignition sources and keep combustibles away from the spill.

At this point, the source of the spill should be identified as quickly as possible. After the source of the release has been identified, further protective actions may be taken. The choice of protective options for a given situation depends on a number of factors. For some cases, evacuation may be the best option; in others, in-place protection may be the best course. In any emergency, officials need to give instructions to the public promptly.

Factors Determining Effectiveness of Evacuation or In-Place Protection

Hazardous Material

- Threatened Population
- Weather Conditions

A table is provided on the website to determine the risk factors and corrective action depending on the size and nature of the spill.

Identify the Pollutants

The Resource Conservation and Recovery Act (RCRA) establishes guidelines for classifying and disposing of hazardous materials. Any release of a potentially hazardous material should be dealt with as described in the operator's spill response plan. Always consider any health effects or immediate environmental impacts associated with the release of a pollutant. RCRA hazardous waste criteria are not the only criteria applicable, other sources such as the Occupational Health and Safety Administration (OSHA) and the national Institute of Occupational Health and Safety (NIOSH) should also be consulted.

Guidelines can be clicked on the website to help in the identification of the pollutant through solid or liquid waste to hazardous waste or mixtures.

Hazardous Waste Characteristics

- Ignitability discusses three categories of liquid and gas that are flammable.
- Corrosivity categorizes a hazardous waste by the rate is corrodes steel.
- Reactivity categorizes a solid hazardous waste by how it reacts with water, other chemicals and temperature changes.
- Toxicity discusses the concentration limits of solid toxic materials.
- Storage container discusses types of containers and handling of full and empty containers.

Remediation Methods

For the petroleum industry the remediation section is limited to crude oil or salt/brine contamination. Improving cleanup methods to increase safety, lower costs, and increase compliance with environmental regulations is an ever-changing

process. This section of ECAS presents information about established emerging remediation/treatment technologies and methods for the cleanup of crude oil and or brine releases resulting in soil or water contamination. Coordinate the remediation of contaminated soil or water with regulatory agencies. Contacting regulatory agencies will assist you in identifying the cleanup requirements. Cleanup requirements and remediation methods/technologies are determined by site-specific factors and the specifics of the contamination, such as:

- Type of contamination
- Extent and volume of contamination
- Use of property
- Age of contamination
- Specific location and adjacent property
- Cost of Remediation

The ECAS website can be linked from the National Petroleum Technology Offices website:

http://www.npto.doe.gov or at the Environmental compliance Assistance System website:

http://www.ecas.ws/index2.htm The ECAS website was prepared by Advanced Integrated Management Services, Inc. for Oak Ridge National Laboratory and the National Petroleum Technology Office.



U.S. Department of Energy National Energy Technology Laboratory National Petroleum Technology Office

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Upcoming Events/Meetings

July

Jul. 12, 2001, Bureau of Land Management, National Petroleum Forum, Sacramento, CA. www.blm.gov/nhp/index.htm

Jul. 17, 2001, Federal Agency Oil & Gas Environmental Research, Technology Stakeholders Input Meeting, Las Vegas, NV. Excalibur Hotel. www.npto.doe.gov/bpo-cal.html

September

Sep. 22-26, 2001, Ground Water Protection Council, 2001 Annual Forum, Reno, NV. www.gwpc.org

November

Nov. 6-9, 2001, Eighth
Annual International
Petroleum Environmental
Conference (IPEC), Issues
and Solutions in Exploration,
Production, and Refining,
Houston, TX.
Renaissance Houston Hotel.
www.ipec.ens.utulsa.edu



